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Wax Coatings for Paper Packaging Applications: Study of the Coating Effect on Surface, Mechanical, and Barrier Properties

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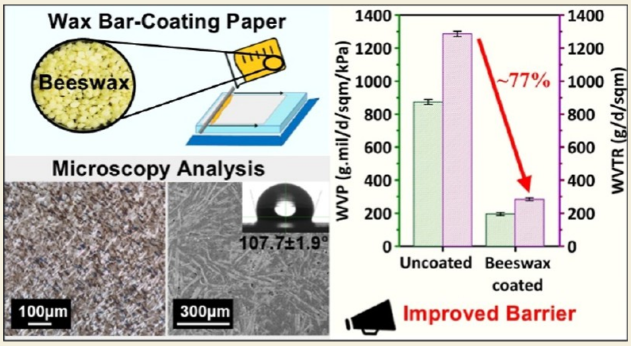
ABSTRACT: The aim of this study was to comprehensively assess the effect of environmentally friendly wax coatings, including beeswax, soywax, TopScreen biowax, and a conventional water-based emulsion wax on paper for food packaging applications. A food-grade paper was bar-coated with a single layer of molten wax on both sides, varying in the coating weight, coating thickness, and wax type. Waxes were thoroughly characterized in terms of their functional groups, thermal properties, degree of crystallinity, and crystal morphology using polarized optical microscopy. Thereafter, wax-coated papers were studied in terms of their morphological, mechanical, and water vapor barrier properties. Moreover, the water and oil contact angles were measured to determine the resistance of wax-coated papers to moisture and grease penetration. Wax coatings represent 10−25% of the weight of the coated paper, with a coating thickness of 5−10 μm. Scanning electron microscopy images showed that waxes penetrated the cellulosic fibers of the paper, thereby effectively reducing its porous structure. Water and oil contact angles of the uncoated paper increased after the wax coating. Among the four waxes, beeswax-coated paper was characterized as having superior capability in improving the water vapor barrier of the uncoated paper (by ∼77%). While the percentage elongation at break (EB %) decreased for all four wax-coated papers, tensile strength (TS) and elastic modulus (E) increased, with beeswax showing the highest percent improvement in TS (by ∼26%) and E (by ∼46%). Our results suggest that paper surface modification through ecofriendly wax coatings can be utilized as an alternative for petroleum-based paper coating materials for food packaging applications.



KEYWORDS: *paper, cellulose, wax, coating material, barrier properties, food packaging*

1. INTRODUCTION

According to the Global Packaging Market report (2018), paper and paperboard account for about 30% of total packaging,[1] making paper a key material in the food packaging sector due to its recyclability, biodegradability, and printability.[2,3] It is widely used in products like baking paper, ice-cream cups, milk cartons, and fast-food containers.[4] Approximately 141 million tons of packaging waste was produced, accounting for 47% of the total waste generated in 2015.[5] Plastic waste, which can break down into harmful microplastics,[6] underscores the urgent need to shift from single-use, petroleum-based plastics to more sustainable, biodegradable options like paper-based packaging.

Plain paper cannot be used alone for applications in food packaging due to its poor barrier properties against oxygen and water vapor and low strength and heat sealability.[4] To improve its performance, strategies include (A) impregnation with fillers (clay, calcium carbonate), retention aids (cationic starch, carboxymethyl cellulose), sizing agents (wax emulsions, styrene acrylate), and wet strength agents (melamine formaldehyde, epichlorohydrin); (B) coating with petroleum-based polymers like polyethylene (PE), polyethylene terephthalate (PET), per- and polyfluoroalkyl substances (PFAS);[7] and (C) metallization.[8]

Coating technology, in particular, has gained attention for enhancing paper's suitability for food packaging. However, coating paper with nonbiodegradable plastic eliminates paper biodegradability and repulpability.[9] Therefore, coating bio-based and biodegradable materials on the paper is a solution to maintain the paper biodegradability toward development of sustainable packaging materials. Various coating techniques can be used for paper-based substrates such as extrusion, size press, curtain lining, bar, and dip coating.[10] Among

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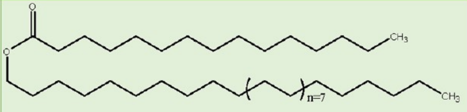
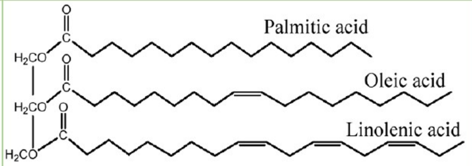
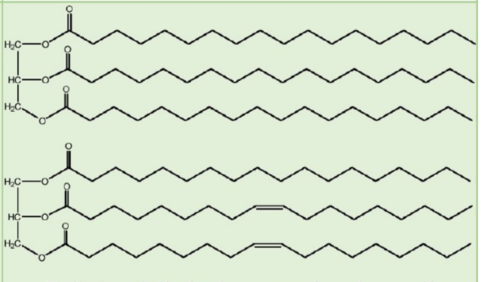
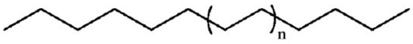
Table 1. Characteristics of Waxes Employed in This Research Study[c][28−34]

Wax	Composition and properties	Major wax/ wax source constituents
	- Beeswax is classified as an animal-based lipid material - The main component of beeswax is myricyl palmitate and cerotic acid. Also, it contains linear monoesters (35%) of long chain (C30-C32) aliphatic alcohols with palmitic acid (C16-saturated) and oleic acid (C18-unsaturated containing C=C)[28, 29] - Physical state at room temperature: Solid - Molten state*: <1min (38s) Supplier: Carmel Industries, Canada	 Myricyl palmitate
	- TopScreen Biowax is classified as a plant-based lipid material. - Based on TDS**, biowax is derived from 100% vegetable raw materials, certified compostable according to EN 13432 - Vegetable-oil based waxes are commonly made through chemical modification (i.e., transesterification, epoxidation and hydrogenation) of triacylglycerols as the main constituent of vegetable oils (>95%)[30, 31] - Physical state at room temperature: Solid - Molten state: ~ 4.5 min Supplier: Solenis, United States of America	 Triacylglycerols
	- Soywax is classified as a plant-based lipid material. - Soywax derived from fully or partially hydrogenation of soybean oil[32, 33] - Physical state at room temperature: Solid - Molten state: ~ 7 min Supplier: Amazon.ca (Brand: Golden Foods)	 Fully/partially hydrogenated soybean oil
	- Chemical name Paraffin wax ≥ 30 - < 40 %w/w , completely miscible in water (based on TDS** "actual concentration is withheld as a trade secret") - Generally, paraffin wax is mainly saturated n-alkanes composed of linear chain hydrocarbons (C10-C40)[30, 34] - Physical state at room temperature: Liquid - Supplier: Solenis, United States of America	 Straight chain n-alkane

[a]The time that the molten wax remains in the liquid phase, which is suitable for the coating process before it solidifies at room temperature. [b]Technical data sheet. [c]The following chemical structures are redrawn by authors, using ChemDraw: Myricyl palmitate. Triacylglycerols, fully/partially hydrogenated soybean oil and straight chain *n* alkane.

biopolymers, lipid materials such as waxes and long-chain fatty acids possess high hydrophobicity and low polarity.[11] This makes them a promising solution for paper coating applications to reduce moisture permeation of the base paper.[12] In addition, wax and cellulose fibers can be easily separated during paper repulping, which has made wax coating paper a commercial interest.[13]

Several studies have explored the effects of wax-incorporated coatings on paper-based substrates. For example, a dual coating of chitosan or zein (first layer) and beeswax (second layer) on paper enhanced water vapor resistance and grease repellency with water vapor transmission rate (WVTR) as low as 52.8 g/m^2/day achieved using 3 wt % chitosan and 4.9 g/m^2 beeswax.[14] In another study, beeswax alone reduced the WVTR to 396.0 g/m^2/day, further decreasing to 195.6 g/m^2/day when the beeswax coating was stabilized with a dimethylglycine (Gly) component.[15] However, interactions between beeswax and other coating components may impact

Figure 1. Experimental methodology; preparation of waxes and coating on the paper. The natural appearance of waxes as well as the molten waxes and wax-coated papers is shown: (a) uncoated paper and (b) biowax-, (c) beeswax-, (d) soywax-, and (e) emulsion wax-coated paper. The emulsion wax is shown as an example for the coating process.

biodegradability and repulpability, requiring further research. Beeswax in water (10 wt %) emulsion coatings with high concentration of cellulose nanofiber (0.6–0.9 wt %) and glycerol as stabilizers resulted in a hydrophilic surface. The water contact angle (WCA) of 96° and water vapor permeation (WVP) of <100 g/m^2/day remained inferior to PE-coated paper.[16]

A beeswax-silica dispersion was spray-coated on gelatin-deposited paper composites for food/drink containers to reduce liquid waste. The subsequent annealing resulted in loss of hydrophobicity, forming a rice-leaf-like structure that allowed liquids like yogurt to roll off.[17] In contrast, 12 h annealing of a paper-coated with beeswax-carnauba wax emulsion converts it from a hydrophobic to "lotus" state, increasing the WCA from 110° to 145°.[18]

Paper immersion in a beeswax-Ag/cellulose nanocrystal composite coating improved the WCA to 113.1°.[19] Paper-coated with a three-layer barrier composed of cationic/anionic nanofibrillated cellulose and a biowax emulsion had a WVTR of 67.1 g/m^2day. However, paper-coated with only biowax showed cracks, resulted in unmeasurable WVTR.[20] Incorporating 10 wt % beeswax into the UV-curable linseed oil paper coatings reduced the WVTR to 20 g/m^2 day and increased the WCA to 111°. After removal of the linseed oil coating, the paper could be repulped by immersing in glacial acetic acid.[21]

In another study, corrugated cardboard was submerged in soybean oil-based wax as an alternative to paraffin wax. The soybean oil-based waxes had a lower WCA of 82° or 95° compared to paraffin wax (103°) due to the interaction of the polyether group in the fatty acid with water. Adding of 5 wt % hydrophobic silica nanoparticles did not significantly affect the bending strength or wetting resistance compared to paraffin.[22] Compounded emulsions made from soybean oil-based wax and commercial acrylic-, polyurethane-, and styrene butadiene-based emulsions reduced the 5 min Cobb value of the paper and showed no grease resistance with a single-layer coating. However, by increasing the coating drawdowns, the grease resistance increased.[13] A microcrystalline wax emulsion coating on starch-pretreated paper increased the paper's oil resistance but reduced the WCA. By increasing the coating load to 6 g/m^2, the Kit rating rose to 10/12, the Cobb$_{60}$ value reduced by 84%, and the WVP decreased by 81.9%, compared to uncoated paper.[23]

Modification of cellulosic paper by coating technology creates products that help extend the food shelf life. Unlike natural cellulose, modified cellulose undergoes changes in morphology or functional groups, raising safety concerns when in contact with food.[24] While microscale cellulose products (e.g., carboxymethyl cellulose, methylcellulose, and hydroxypropyl cellulose) are "generally regarded as safe", nanocellulose is not yet considered safe for food applications.[25,26] Therefore, the safety of nanocellulose must be thoroughly evaluated for use in the food industry.

Our literature review revealed a limited focus on studies exclusively employing environmentally friendly wax as a coating using a facile method to enhance the water vapor barrier properties while preserving paper's satisfactory mechanical performance and biodegradability, which is supported by (I) and (II):

(I) The predominant trend has been toward using wax emulsions or combining wax with substances like cellulose nanocrystals or linseed oil or coating wax on a pretreated paper by chitosan, zein, or starch. However, adding these substances increases processing time and costs and requires careful optimization of emulsifier/biopolymer ratios, which affects coating stability and performance, such as water and grease resistance.

(II) On the other hand, some studies have used multilayer coatings for better performance of a paper substrate,[13,27] but this approach is time-consuming, requires more materials, and increases coating weight. This is contrary to the industry's desire for lighter, more cost-effective packaging solutions to reduce packaging materials.

In this study, we performed a simple one-time wax coating as a hydrophobic material on paper by using a bar-coating technique. Diverse ecofriendly waxes and a conventional wax were used, and the effect of coating was investigated through a water vapor barrier, water/oil contact angle, grease resistance, and morphological and mechanical properties. The nature of waxes was also studied by thermal properties, crystal morphology, and degree of crystallinity as well as Fourier transform infrared (FTIR) spectroscopy. The purpose of applying a thin, uniform layer of wax on the paper substrate, instead of increasing the wax coating weight through multiple layers, is to preserve the substrate's mechanical strength while also improving its inadequate water vapor barrier properties.

2. EXPERIMENTAL SECTION

2.1. Materials

The characteristics of the waxes used in this study are shown in Table 1. The purchased waxes were used without any additional modifications. For simplicity, Water emulsion wax and TopScreen biowax are referred to as emulsion wax and biowax, respectively, throughout the paper. Silica gel was used as a desiccant, and was obtained from Sigma-Aldrich (Canada). Deionized water (ASTM Type II), obtained from Fisher Scientific, was used to maintain the relative humidity during the WVP analysis. The stainless-steel spiral wire bar coater (Figure 1) was supplied by Industrial Physics, USA, with specifications of a 320 mm film width and 4 μm thickness. The food-grade-quality Kraft Butcher paper (white color) manufactured by YRYMHT, China, was purchased from Amazon, which was unwaxed and uncoated with a weight per unit area of 40 g/m^2. A commercial wax-coated paper (Reynolds Kitchens Cut-Rite Wax Paper) was purchased from the supermarket to compare its water vapor barrier properties to those of wax-coated papers prepared in this study.

2.2. Methods

2.2.1. Coating Waxes on the Paper. A beaker containing granules of wax (beeswax or biowax or soywax) was enclosed by aluminum foil and placed in a silicon oil bath set at 75 °C to obtain molten wax with appropriate viscosity for even coating. Papers were cut into 10 cm × 20 cm square pieces. To identify the most suitable paper type to minimize the wax coating weight, preliminary experiments were conducted by coating the wax on three different paper types (white printing paper, brown Kraft paper, and white Kraft Butcher paper). Keeping the wax type and coating conditions the same, Kraft Butcher paper showed the lowest wax coating weight, and thus, it was chosen for further study and characterizations. The temperature of the melted wax was sustained at 75 °C for approximately 20 min, monitored by a thermometer until the waxes were melted completely. The molten wax was coated one time on both sides of the paper with the spiral wire bar coater. The wax coating on the paper was replicated at least three times to ensure reproducibility and repeatability. In the case of emulsion wax, it was used as it is in liquid form. The wax was poured onto the paper, fixed at one end on a hot plate (60−70 °C), and kept in contact with the bar. The bar was drawn down manually with a consistent speed, and a coating layer was formed on the paper. The thickness of the layer depends on the amount of wax poured on the paper and the bar coating thickness (here, a 4 μm bar was used). The 2-sided-coated paper was kept for 15 min at room temperature and then hung vertically for 3 h in an oven at 75 °C so that excess wax drained from the paper (Figure 1). The weight % of wax coating (with respect to the substrate's mass) was calculated based on eq 1.[35] The thickness of the wax coating was determined by measuring the difference in total thickness between cross sections of uncoated and wax-coated paper by using scanning electron microscopy (SEM). Overall, the wax coating showed a thickness of 5−10 μm. For coating thickness, at least 5 measurements were performed at different positions along the width and length of the wax-coated papers. For the wax coating weight, at least 3 samples were measured with the average reported. The wax coating weight and total thickness (wax-coated paper) are shown in Table 2.

$$\text{Coating weight \%} = \frac{\text{coated paper}\left(\frac{\text{g}}{\text{m}^2}\right) - \text{uncoated paper}\left(\frac{\text{g}}{\text{m}^2}\right)}{\text{uncoated paper}\left(\frac{\text{g}}{\text{m}^2}\right)} \times 100 \quad (1)$$

Table 2. Total Coating Thickness and Weight % of Wax-Coated Papers

sample	total thickness (μm)	coating weight %
uncoated paper	90.30 ± 3.24	None
beeswax-coated paper	95.32 ± 2.73	24.9 ± 5.6
biowax-coated paper	95.40 ± 3.49	20.6 ± 3.1
soywax-coated paper	100.70 ± 3.06	24.2 ± 5.1
emulsion wax-coated paper	97.82 ± 5.82	10.1 ± 0.02

3. CHARACTERIZATIONS

3.1. Fourier Transform Infrared Spectroscopy

Attenuated total reflectance-FTIR spectra (Nicolet 6700, Thermo Fisher Scientific, USA) were used to identify the functional groups that were present in four types of waxes used in this study. The spectra within 4000 to 400 cm^{-1}

wavelengths through 64 scans and a resolution of 4 cm^{-1} were used for analyzing the samples.

3.2. Thermal Properties

Thermal stability assessment of waxes was carried out through thermogravimetric analysis (TGA) utilizing a TG Q500 instrument (TA Instruments, USA). In a nitrogen-enriched environment, samples were placed in a platinum pan and heated at a rate of 10 °C/min, ranging from 30 to 700 °C.

Differential scanning calorimetry (DSC) analysis was performed with a TA Instruments DSC Q200 (USA) instrument to investigate the thermal properties of waxes. This included determining the melting temperature (T_m), crystallization temperature (T_c), and glass-transition temperature (T_g). Samples with weights ranging from 15 to 20 mg were enclosed in an aluminum hermetic pan under N_2. The heating programs comprised a 10 °C/min rate from −50 to 120 °C, followed by cooling to −50 °C at a rate of 5 °C/min and then heating to 120 °C. Lastly, the software TA Instruments Universal Analysis 2000 (4.5A version) was used to analyze the TGA and DSC curves.

3.3. Polarized Optical Microscopy

To analyze the crystalline morphology of waxes, a Universal Design Nikon Microscope (Tokyo) with polarized optical microscopy (POM) and a Linkam hot stage for sample preparation were employed. Photographic images were studied with the software NIS-Elements BR2:3 SP2 (Build 361). Subsequently, the samples were melted by heating to a predetermined temperature and then cooled under liquid N_2 to a predetermined temperature to observe wax crystallization. The predetermined temperatures were chosen based on melting and crystallization temperatures observed in the DSC analysis, which are listed in Table 3. The samples were maintained at the cooling temperature for 25−30 min before capturing microscope images.

Table 3. Heating and Cooling Temperature Program in POM with the Rate of 10 °C/min

wax	heating temperature (°C)	cooling temperature (°C)
beeswax	80 ± 2	45 ± 2
biowax	65 ± 2	40 ± 2
soywax	55 ± 2	20 ± 2
emulsion wax	75 ± 2	50 ± 2

3.4. X-ray Diffraction Spectroscopy

The structures of crystals and polymorphic forms of the pure waxes were analyzed using a powder X-ray diffractometer (MiniFlex 300/600 Powder X-ray diffraction (XRD) spectrometer, Rigaku, Tokyo, Japan). The copper X-ray tube operated at 40 kV and 15 mA. Measurements were taken at a scan rate of 5° per minute within the 2θ range of 10−80° at a temperature of 20 °C. The percentage crystallinity of waxes was calculated using eq 2,[36] where P_C is the integrated area underneath the crystalline peaks and P_T is the total integrated area underneath the XRD pattern.

$$\% \text{ Crystallinity } (\lambda_{\text{C,XRD}}) = \frac{P_C}{P_T} \tag{2}$$

3.5. Scanning Electron Microscopy

The surface morphology of wax-coated papers was examined by Phenom World BV (the Netherlands) SEM at 10 kV. Specimens were immersed in liquid N_2 and manually fractured with a hammer and a chisel. Using a carbon tape, the surface and cross section of the samples were mounted on SEM stubs. Then, to avoid charging during imaging, samples were sputter-coated with gold. To assess thickness and coating uniformity on the paper, a minimum of three samples used for each type of wax-coated paper and uncoated paper and measurements were taken from various positions along the width and length of the sample.

3.6. Mechanical Properties

The mechanical properties of both paper and wax-coated paper were analyzed by an Instron 3382 universal testing machine (USA) under conditions of 23 °C and 50% relative humidity in accordance with standard ASTM D882-18. Specimens were cut to 175 mm × 20 mm squares pieces and were positioned between the two grips with a 125 mm gauge length in the tensile testing machine. Five test samples were analyzed for each type of wax-coated paper. Prior to characterization, all samples were kept at a relative humidity of 50 ± 10% and temperature of 23 ± 2 °C for a duration of 48 h.

3.7. Water and Oil Contact Angle

The WCA of wax-coated papers was determined with a ramé-Hart standard goniometer (260-U1, USA). A water droplet of 5 μL was placed on the specimen (2 cm × 2 cm squares) using a glass syringe. The DROP image advanced software was utilized to measure the contact angles of left and right, and the average is reported. The test was performed with 0.01° resolution and ±0.1° accuracy at 0° stage position. Three samples were analyzed for each kind of wax-coated paper, and different areas of each wax-coated paper and uncoated paper were used to cut the sample. The oil contact angle was measured with the same conditions by using a micropipet to drop 2 μL of corn oil on the paper.

3.8. Oil Absorption and Spreading

To assess the oil-repelling capacity of wax-coated paper, the spreading and absorption of corn oil were investigated. Three samples were tested for each type of wax-coated paper. Samples were cut into 5 cm × 5 cm square pieces, and 2 μL of corn oil was carefully deposited onto the paper surface using a micropipette. After 8 h period, any remaining oil on the paper surface was wiped off with a clean tissue, and the weight percentage of oil absorption was calculated using eq 3. In order to simulate practical applications of wax-coated papers for ready-to-go food, boxes were assembled with wax-coated papers and filled with fried potatoes purchased from the market. Subsequently, the spreading of oil through the box containing fried potatoes was studied over 24 h duration.

$$\begin{aligned} \text{Oil absorption weight \%} = {} & [1 - ([\text{Paper weight after wiping oil} \\ & - \text{Paper weight before wiping oil}]/[\text{weight of total oil}])] \times 100 \end{aligned} \tag{3}$$

3.9. Water Vapor Barrier Properties

The wax-coated paper was evaluated in terms of their barrier against water vapor using the cup method (ASTM E96/E96 M-22). Testing was conducted with a sample area of 127 cm^2, at 37.8 °C and 90 ± 5% relative humidity. The sample was securely positioned in an aluminum cup as illustrated in our previous work.[35] Each cup, with a diameter of 6.36 cm, contained ∼25 g of silica gel as a desiccant. An environmental chamber was used (Advanced eco Peltier Technology

Memmert, Germany) to put the cups inside for a 90 min period to ensure stabilization before weighing. The weight of the cups was continuously measured until a minimum of eight readings were recorded. Following this step, calculations were performed to determine both the water vapor permeability (WVP) and the water vapor transmission rate (WVTR). Three samples were analyzed for each kind of wax-coated paper and uncoated paper.

4. RESULTS AND DISCUSSION

4.1. Analysis of Waxes

4.1.1. Fourier Transform Infrared Spectroscopy. Waxes are generally esters of long fatty acids (C16−C36) and long chain alcohols. Typically, beeswax is composed of a mixture of free fatty acids, free fatty alcohols, and mono- and complex wax esters. Soywax is composed of fully or partially hydrogenated soybean oil (Table 1) as reported elsewhere.[33] Based on the technical data sheet, biowax is derived from 100% vegetable raw materials, and the emulsion wax is a paraffin wax, composed of straight chain *n* alkanes, and it is completely miscible in water. Environmental factors, genetics, and sources of waxes affect their composition. However, the aliphatic skeleton is usually unsaturated and monoenoic (i.e., containing one C═C), except for some marine-origin waxes and waxes from some higher animals (i.e., mammals and vertebrates).[37]

The chemical structures of major wax constituents used in this study are depicted in Table 1 and FTIR spectroscopy of the four types of waxes was performed to investigate their chemical structure and functional groups (Figure 2).

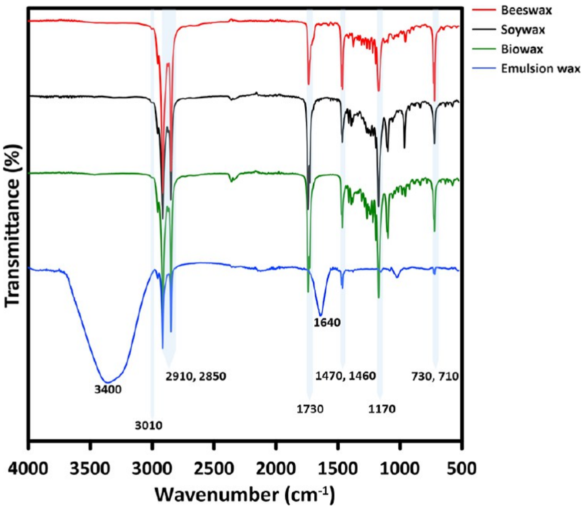


Figure 2. FTIR spectra of beeswax, soywax, biowax, and emulsion wax.

Beeswax, soywax, and biowax showed great similarities in their functional groups. The sharp peak at 1730 cm^{-1} indicated the stretching of the carbonyl ester functional group[38] in these three waxes, which was not observed in emulsion wax. The small weak peak at 3010 cm^{-1} showed the presence of C═C in the CH_2−CH_2 of the acyl chain. The sharp peak at 1170 cm^{-1} corresponds to C−O−C bond[39] or C═O stretching and C−H bending vibrations of esters.[40]

The characteristic peaks that are similar in all four waxes are as follows. The pair of peaks around 1460 and 1470 cm^{-1} indicate the planar deformation vibrations (scissoring) of CH_2 groups,[41] with the pair around 710 and 730 cm^{-1} suggesting an ordered orthorhombic arrangement of the long aliphatic chains.[42] The peaks are specific for a long aliphatic chain and correspond to the rocking vibration of C−H.[43] These two peaks are more intense for beeswax compared with other waxes. Sharp strong peaks at 2910 and 2850 cm^{-1} correspond to the vibration of the aliphatic asymmetric and symmetric CH_2 group,[44] which are visible in all four waxes.

The two characteristic large bands for emulsion wax are the broad and strong peak at 3400 cm^{-1} (stretching vibration of O−H) and 1640 cm^{-1} (bending vibration of H−O−H), which characterized the IR spectrum of ultrapure water.[45] Moreover, the emulsion wax is a paraffin wax emulsion based on the technical data sheet.[46] The peaks are very similar to the paraffin FTIR spectrum observed in the previous literature[47] except for the peaks attributed to the water content in the present water-based emulsion wax.

4.1.2. Thermal Properties. TGA and corresponding derivatives (DTG) were studied to explore the thermal stability of waxes, and thermograms are shown in Figure 3. Thermal stability is a crucial property for wax-containing materials, as the decomposition of the aliphatic chain with increasing temperature can pose a limitation in both processing and application.[48,49] There are several works addressing the importance of wax thermal stability when incorporated into polymers or composites. For instance, incorporating up to 15% palm wax could raise the initial thermal degradation temperature of thermoplastic cassava starch (TPCS) from 295 °C to 308 °C, due to the higher initial decomposition temperature of native palm wax compared to TPCS.[50] Therefore, understanding the thermal stability of a wax at different temperatures is crucial when selecting one for use in polymer blends or composites. Additionally, temperature is a key factor in wax degradation, emphasizing the need for careful storage and transportation of these compounds,[51] such as wax-coated paper used in food packaging applications.

For all waxes, the temperature where a deflection is first observed (i.e., T_{onset}) is around 190−200 °C with the order of $T_{2\%}$ beeswax (209.0 °C) < emulsion wax (220.7 °C) < biowax (228.3 °C) < soywax (256.8 °C). Comparing the maximum temperature, at which the mass loss recedes (i.e., T_{endset}), waxes will be in the order of emulsion wax (382.2 °C) < biowax (423.3 °C) < soywax (455.5 °C) < beeswax (460.4 °C).

Among four types of waxes, soywax showed the greatest thermal stability with the peak decomposition (i.e., T_{max}) at 431.6 °C. On the other hand, emulsion wax showed the lowest thermal stability with a T_{max} at 300.8 °C. The lower T_{max} for the water emulsion wax can be due to its lower molecular weight compared to the other three waxes. Among all waxes, only emulsion wax showed a residual weight fraction (3.3%) after complete degradation, which can be due to the presence of inorganic compounds in the emulsion wax. Among all waxes, beeswax showed two weight losses in DTG, which agrees with the previous literature[52] and is the characteristic of the multicomponent material structure.[53]

TGA of the natural waxes has not been fully explored in the literature. However, it is noteworthy that beeswax has been studied by more researchers, among other natural waxes. Comparing with other waxes in the literature, the microcrystalline wax emulsion showed a T_{max} at ∼350 °C.[23] Moreover, the high thermal stability of soywax compared to the other three waxes resembles the thermal stability of

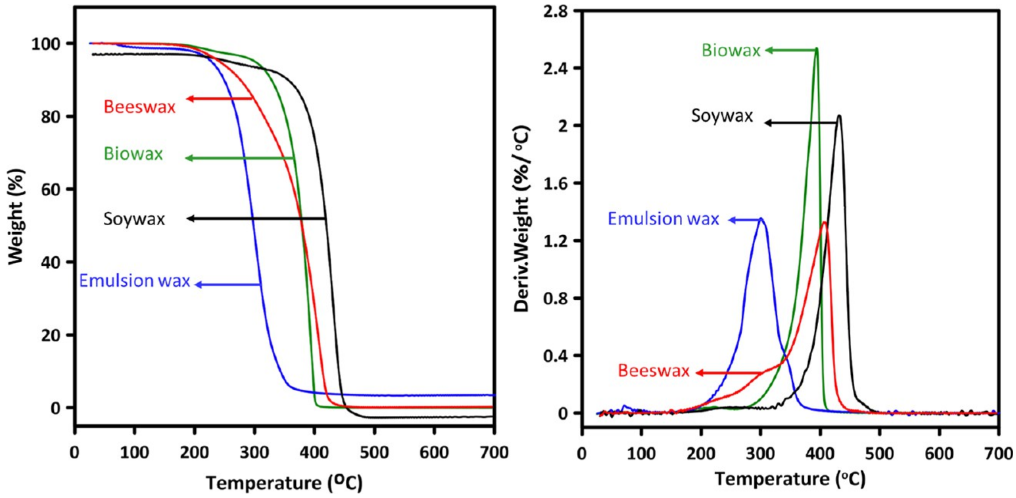


Figure 3. TGA (left) and DTG (right) of four types of waxes.

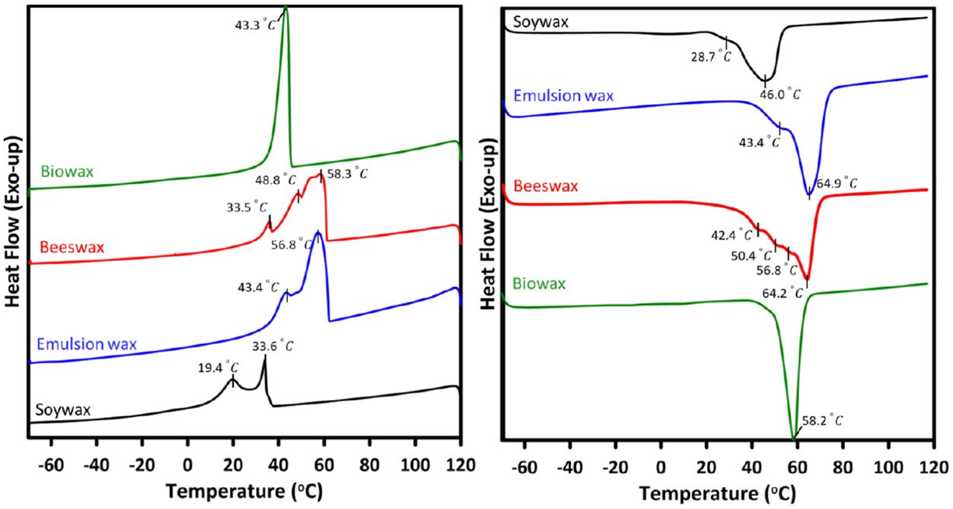


Figure 4. First cooling cycle (left) with labeled crystallization temperatures and second heating cycle (right) with labeled melting temperatures for four types of waxes.

carnauba wax in the previous literature showing a T_{max} at ∼450 °C.[54] Waxes that are used in this study showed higher thermal stability comparing with petroleum-based wax such as paraffin wax, whose T_{onset} was observed around ∼150 °C.[55]

DSC was also investigated to study the melting and crystallization behavior of waxes (Figure 4). All waxes, except for biowax, showed melting and crystallization behavior over a wide range of temperatures, which is in agreement with previous literature.[33] This observation suggests that the waxes experienced polymorphic phase changes during both cooling and melting. Additionally, this indicates that the various mass or component fractions in waxes maintained their characteristic packing behavior upon cooling, leading to crystallization and melting at temperatures specific to each component. The presence of more than one melting peak in DSC indicates the tendency of phase separation of molecules in a material.[56]

Beeswax, emulsion wax, and soywax showed multiple peaks for melting and crystallization temperatures, which are characteristic of multicomponent materials. The quantity and placement of the peaks on the curve suggest the chemical composition of the sample. To be more precise, these peaks likely indicate the melting of different phases, which may consist of single or multiple components. The melting transitions' end points (e.g., 64.2 °C for beeswax) include the melting points of several major components, such as fatty acids and wax esters, that are present in beeswax.[57] Similar multiple melting and crystallization peaks were observed for beeswax,[58] soywax, and carnauba wax[33] in the previous literature. Comparing to petroleum waxes, paraffin wax showed the same behavior as multiple peaks for melting and crystallization.[59]

Beeswax and soywax are biobased waxes with different compositions of esters and fatty acids, which results in varying degree of polarity and intermolecular attractions.[33] This is in agreement with the literature, which reported that the last transition was attributed to solid−liquid transition (melting point at 64.2 °C) of the beeswax components and the peaks before 64.2 °C are attributed to solid−solid transitions.[60] The melting and crystallization peak of soywax is also in agreement with the previous literature.[33]

In contrast to the other three waxes, biowax showed only one single peak for melting and crystallization, which implies a higher component purity or one-phase component in the biowax. Among natural waxes, which are explored in the literature, carnauba wax showed similar behavior to the biowax in the present study, by having a single melting temperature.[61]

Both in academia and industry, DSC analysis has been used to determine the percentage of crystallinity. The crystallinity degree is determined by dividing the melting enthalpy value of a material by the heat required to melt the sample with 100% crystallinity, also known as the heat of fusion. However, the heat of fusion for natural waxes with 100% crystallinity is not available to calculate their degree of crystallinity based on DSC. The melting enthalpy of four waxes is presented in Table 4. Among the four waxes, beeswax showed the highest melting enthalpy, which can correspond to its higher degree of crystallinity. Similar conclusions were made in the literature in terms of higher degree of crystallinity of paraffin wax based on its higher melting enthalpy.[33] In some research papers, the crystallinity of natural waxes was measured relative to the paraffin wax by dividing the melting enthalpy of the natural wax obtained from DSC by the enthalpy of paraffin wax.[62] However, we argue that this is not an accurate method as the composition of natural waxes is more complex than paraffin wax, which contains only *n*-alkane chains. In addition, physical properties such as melting enthalpy of a 100% crystalline natural wax depend on different factors such as the geographic region, weather conditions, etc., which all need to be considered. Therefore, we performed XRD spectroscopy (Section 4.1.3) to calculate the degree of crystallinity for waxes.

Table 4. Waxes' Enthalpy of Fusion Obtained from DSC and Degree of Crystallinity Obtained from XRD

wax	ΔH_m J/g	λ_c (%) from XRD
beeswax	221.0	81.3
biowax	156.2	79.1
soywax	118.20	73.8
emulsion wax	213.20	67.1

4.1.3. XRD Spectroscopy. The XRD spectra of pure waxes are shown in Figure 5. In previous literature, two diffraction peaks at 4.1 and 3.7 Å were observed for crystal structures of plant wax in the wide-angle region (WAXS).[63]

In our study, for beeswax and emulsion wax, the wide-angle X-ray patterns were identical, showing two sharp diffraction peaks at 4.1 Å ($2\theta = 21.5°$) and 3.7 Å ($2\theta = 23.9°$). On the other hand, the biowax and soywax showed similarities in their WAXS region, and the two major peaks were observed at 3.8 and 4.2 Å. The existence of these two major peaks that are present in all four waxes is attributed to arrangements of orthorhombic perpendicular subcell packing in waxes. This crystal structure resembles the polymorphic form of β' crystals in fats.[63] An ordered orthorhombic arrangement of the long aliphatic chains in waxes was also confirmed by FTIR analysis in this study (pair peaks at 1460, 1470 and 710, 730 cm^{-1}). Due to the small size of fat crystals in the polymorphic form of β', this crystal structure exhibits a smooth texture and high spreadability.[64] This property in the wax nature makes it a suitable material for coating applications to be able to spread evenly on the surface substrate, which is a paper in this study. The diffraction peaks at around 3.7 and 4.1 Å correspond to CH_2 in the acyl chain (*n*-alkanes) of waxes,[47] which were observed in all four waxes, and the peak at around 4.6 Å corresponds to oleic acid content in waxes,[47] which were observed in all waxes except for emulsion wax that composed of CH_2-CH_2 chains.

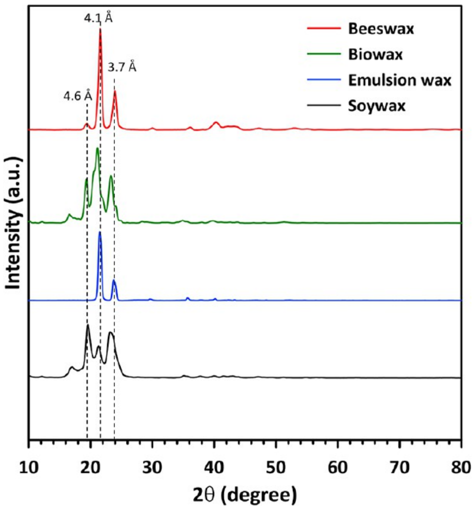


Figure 5. XRD spectra of waxes (as received).

The degree of crystallinity of waxes was also calculated based on eq 2 and the values are listed in Table 4. Beeswax showed the highest degree of crystallinity and, therefore, requires more energy for solid−liquid transition (i.e., enthalpy of fusion in DSC analysis). Biowax and soywax showed degrees of crystallinity in the range of 74−80% and emulsion wax showed the lowest degree of crystallinity.

4.1.4. Polarized Optical Microscopy. The crystal morphology of each wax was studied by using POM. Various molecular rearrangements might occur during crystallization. This molecular rearrangement originates from the formation of crystalline networks, which differ in physical characteristics depending on the types of wax being used and its multicomponent structure. The compositions of the four waxes used in this study were explained earlier in the FTIR section. All waxes were first studied at room temperature and then underwent heat−cool cycles to allow crystal regrowth. The temperature of the heat−cool cycles for each wax is detailed in Table 3.

All four waxes showed crystalline structures at room temperature before the heat and cooling cycles (Figure 6). Beeswax and soywax showed a compact homogeneous crystal formation and the barrier between crystals was not visible. Biowax, on the other hand, showed both small and some very large crystals with visible barriers among them, particularly after cooling down to its crystallization temperature (i.e., 40 ± 2 °C). Emulsion wax showed the lowest compact crystal structures containing multiple irregular voids and spaces between their needle-like crystal structures.

In the literature, it is reported that plant waxes show platelet-like crystals in SEM analysis, which appears to be needle-like in optical microscopy.[65] These needle-like crystals have been better observed in the case of the emulsion wax in this study. One possible reason for the needle-like shape may be that it is merely a perspective of the protruding edge of the platelets. Similar needle-like crystal structures were observed for paraffin wax in the literature,[22] which is very similar to our emulsion wax. The needle-like structure could potentially stem from crystallization taking place on the glass while preparing samples for POM. From a thermodynamic point of view, the crystallization of hydrophobic waxes on the hydrophilic glass is disfavored. When crystallizing the hydrophobic wax along

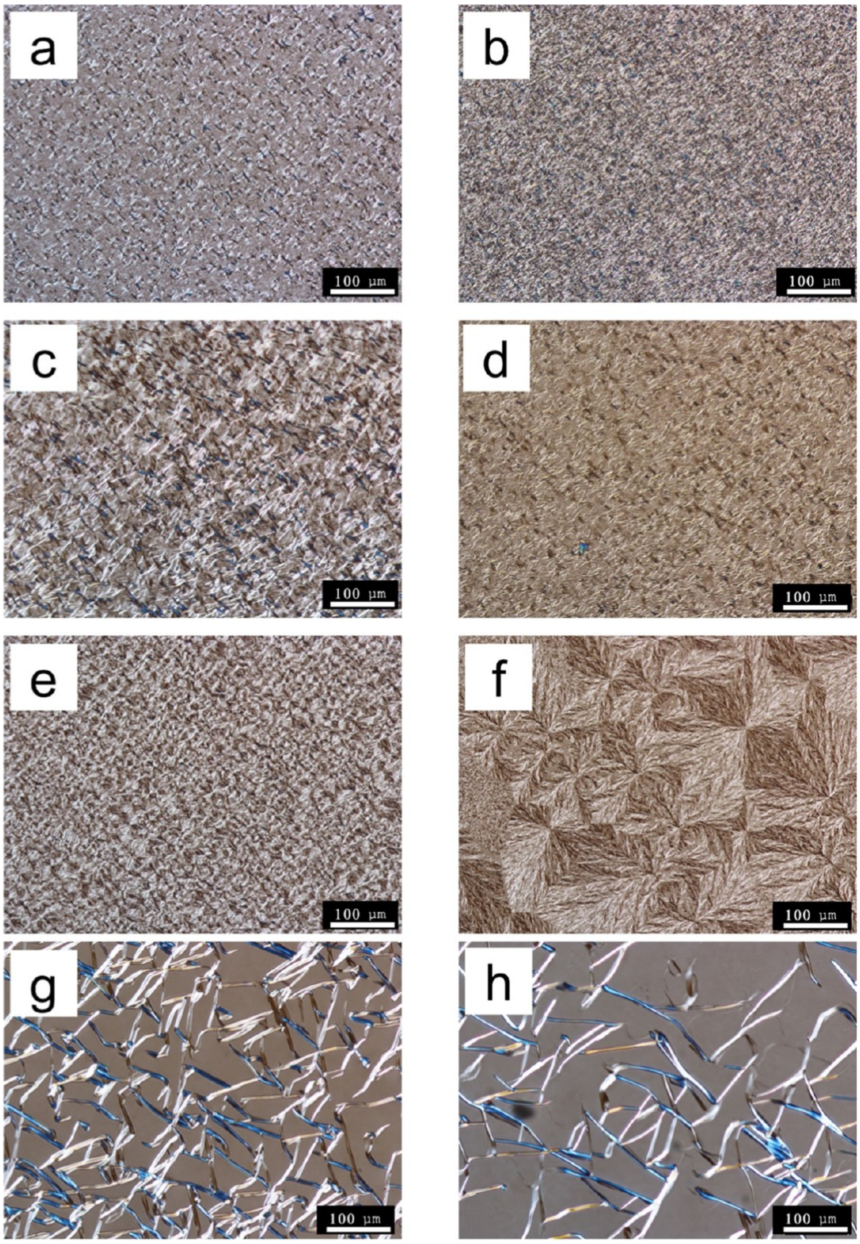


Figure 6. POM of (a,b) soywax, (c,d) beeswax, (e,f) biowax, and (g,h) emulsion wax. Pictures on the left are taken at room temperature and pictures on the right are taken after 25−30 min while keeping waxes at their crystallization temperature.

the edge of a platelet, the contact area to the hydrophilic glass is minimized, consequently leading to the development of a needle-like structure.[66]

Based on the previous literature, fine and more compact crystal structures contribute to smooth coatings with less defects (e.g., pores, cracks, etc.).[67] In the present study, beeswax, soywax, and biowax showed finer crystals, which were also reported elsewhere,[62] compared to the needle-like structure of the emulsion wax. Similar crystal morphologies were observed in the previous literature for natural waxes.[67]

Most of the aforementioned studies focused on the crystal morphology of waxes when they are blended with other waxes or oils. Martini et al.[68] concluded that the T_c, cooling rate and wax concentration of the sample are main parameters that affect the crystal morphology of waxes in a blend. We believe that the study of pure natural waxes in this paper can lead researchers to obtain a better understanding of each wax crystal morphology to further the selection and usage in desirable applications.

4.2. Analysis of Wax-Coated Papers

4.2.1. Scanning Electron Microscopy. The morphology of surface wax-coating and the coating uniformity was investigated by SEM (Figure 7). The uncoated paper compared to wax-coated papers showed a porous structure within cellulose fibers, which is the characteristic of cellulosic substrates and has been observed in the literature.[23] However, after wax-coating, the paper surface appeared to be less porous and more sealed, which was also observed in the previous literature after coating paper with tempo-oxidized cellulose nanofiber and beeswax emulsions[16] or microcrystalline wax.[23]

Among wax-coated papers, beeswax and emulsion wax coatings showed a more uniform layer by filling within the cellulose fibers, which also resulted in a smoother paper as

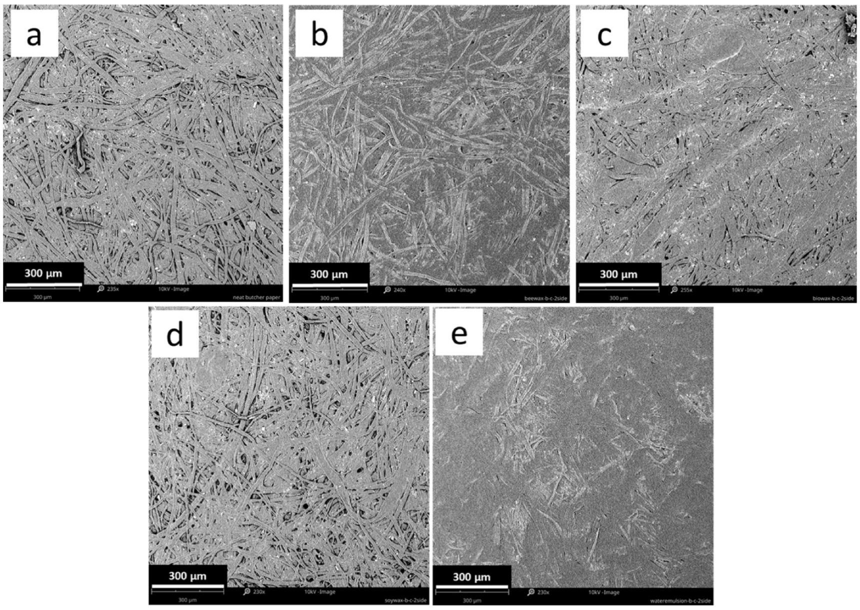


Figure 7. SEM of the surface of uncoated paper and wax-coated papers. (a) Uncoated paper, (b) beeswax-coated paper, (c) biowax-coated paper, (d) soywax-coated paper, and (e) emulsion wax-coated paper.

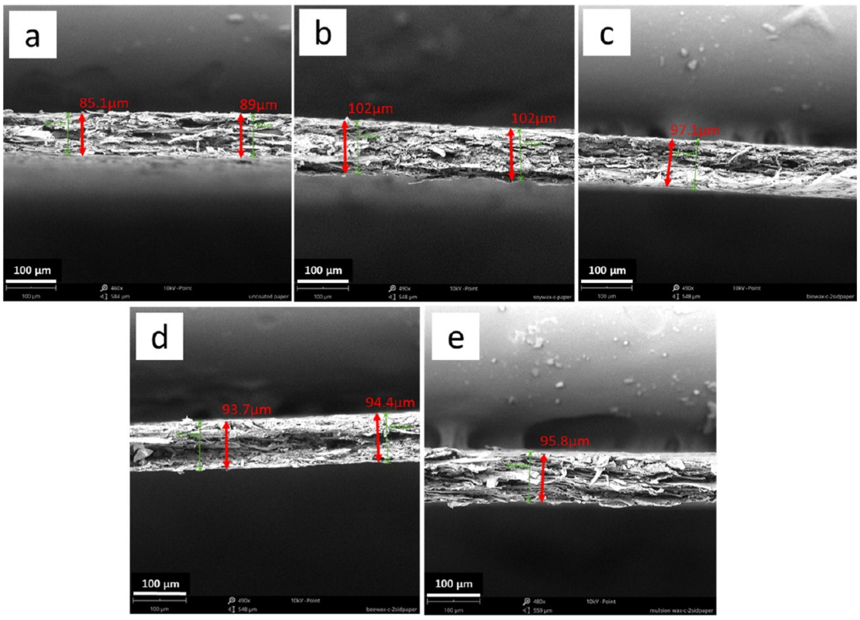
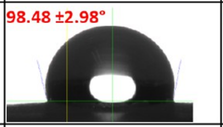
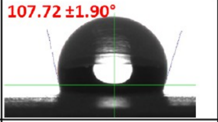
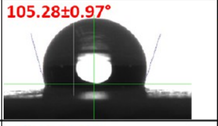
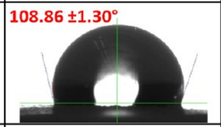
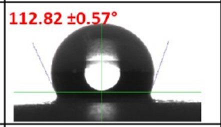
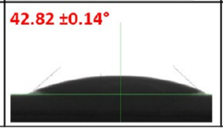
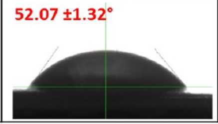
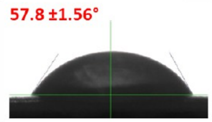
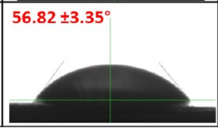
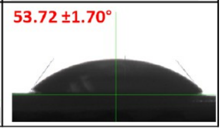


Figure 8. SEM of cross section for wax-coated papers. (a) Uncoated paper, (b) soywax-coated paper, (c) biowax-coated paper, (d) beeswax-coated paper, and (e) emulsion wax-coated paper.

compared to the uncoated paper. The same observation is reported in the literature for a beeswax-poly(hexamethylene guanidine hydrochloride) latex coating on paper.[15] With the same amount of coating weight, beeswax-coated paper in this study showed a smoother surface than those observed in the literature for $AgNO_3$/beeswax/CNC nanocomposite coating on the paper.[19] In the case of biowax and soywax coating, the paper surface was covered with the wax, but the paper still maintained its porous structure, with higher pores seen for soywax-coated paper compared with biowax-coated paper. More uniform coating, which is a result of complete filling of the cellulose fibers and pores with a layer of wax, led to a higher WCA and higher water vapor barrier properties of wax-coated papers compared to those of the uncoated paper, which will be discussed in the following sections. No cracks were observed on the surface coating of the four waxes in the present study, in contrast with the previous literature that coating paper with only a natural wax resulted in a surface with multiple cracks.[20]

The coating procedure and coating temperature, viscosity of molten wax (i.e., having enough flowability for the coating process), and uniform coating thickness all over the surface are crucial parameters to obtain a final uniform coating on the paper substrate. We performed preliminary studies to optimize these parameters in order to obtain a uniform coating, which further resulted in enhanced hydrophobicity and a barrier against WVP. In the present study, we used a bar coater to manually coat both sides of the paper. The user's hand speed

Table 5. Water/Oil Contact Angle measurements on the Uncoated and Wax-Coated Papers

Contact angle	Paper	Beeswax-coated paper	Biowax-coated paper	Soywax-coated paper	Emulsion wax-coated paper
Water	 98.48 ±2.98°	 107.72 ±1.90°	 105.28±0.97°	 108.86 ±1.30°	 112.82 ±0.57°
Corn oil	 42.82 ±0.14°	 52.07 ±1.32°	 57.8 ±1.56°	 56.82 ±3.35°	 53.72 ±1.70°

and the applied pressure while drawing down the bar coater on the substrate are optimized to achieve a uniform wax coating. All waxes, except for emulsionwax, melted in an oil bath, and the coating process was performed right after the wax melted completely. Keeping the molten wax for a long time inside the oil bath results in a reduction of its viscosity. This ends up with a nonuniform thin layer on the paper surface and curling of the paper because of the higher absorption of the wax by the cellulose fibers (i.e., higher final coating weight). This is not desirable from a sustainable perspective for lightweight packaging materials.

To study the wax coating thickness on the paper substrate, the wax-coated papers were studied through the cross section in a SEM instrument (Figure 8). The coating thicknesses for wax-coated papers are summarized in Table 2. Waxes impregnated into the paper fibers, and thus, a distinguished layer of wax-coating on both sides of the paper was not fully detectable and could not be accurately measured. Therefore, the wax coating thickness is measured by calculating the thickness difference between uncoated paper and wax-coated paper for each of the four waxes. Overall, waxes showed a coating thickness in the range of 5−10 μm.

Although wax-coatings in this study did not show a separate coating layer on the paper substrate, the morphological properties of surface coatings were similar to those observed for paraffin wax emulsion-coated papers reported in the previous literature in terms of formation of a more homogeneous and smoother surface compared to uncoated paper.[34]

4.2.2. Contact Angle—Water and Oil. Contact angle analysis was performed to investigate the hydrophobicity (using water) and oleophobicity (using corn oil) of wax-coated papers compared to uncoated papers, and the results are summarized in Table 5. A greater WCA shows a greater hydrophobicity of the surface.[69] In the case of beeswax, soywax, and biowax, the WCA improved slightly by around 7−10%, while emulsion wax improved the WCA by ∼15%. Based on the FTIR analysis (Figure 2) and the chemical structure of the emulsion wax (Table 1), it is a straight chain alkane. Thus, the higher contact angle of emulsion wax-coated paper can be due to its hydrophobicity and absence of polar groups such as COO− and C−O−C.

In the present study, the coating weight of waxes for biowax, soywax, and beeswax is in the range of 20−25 g/m^2, except for emulsion wax, whose coating weight is around 10 g/m^2. Preliminary studies were also performed to increase the coating weight of, particularly, emulsion wax. However, it was not desirable as it resulted in a nonuniform coating and curling of the paper possibly due to a higher absorption of the wax by the paper. Although the coating weight in this study was similar to what was reported in the literature,[15] the contact angle of wax-coated papers was lower than that of beeswax-poly(hexamethylene guanidine hydrochloride) (PHGH)-coated paper. However, the contact angle achieved in this study with only one time coating on both sides of the paper was higher than those reported for nanocellulose-stabilized beeswax suspension-coated paper,[16] acrylated linseed oil 5 wt % beeswax-coated paper,[21] cellulose sheet dip-coated with carnauba wax micro- and nanoemulsions with multiple times of coating,[27] soybean oil-based wax-coated paper,[22] and paraffin wax-coated papers.[34]

Comparing the WCA of some polysaccharide-based and protein-based coatings on the paper, the contact angle of wax-coated papers prepared in this study was higher than those of glucan-natural rubber-coated papers[70] and was comparable with those of wheat gluten-coated paper with calcium carbonate and starch[71] showing the potential ability of lipid-based materials in reducing the hydrophilicity of the paper.

The information above indicates the high capability of natural waxes (used in this study) and, particularly, beeswax alone in forming a rough surface and reducing the surface energy of the paper substrate, which makes wax-coated papers suitable for hydrophobic food packaging applications.

As the paper substrate is a porous material, it has low resistance against water and oil due to the presence of pores which offer routes for water and oil to transfer.[5] The ability to resist grease (oleophobicity) is another essential property needed for paper packaging intended for food products, such as butter wrappers, baking papers, and wraps used in fast-food industries (e.g., for meat, burgers, and fries). The oil contact angle of wax-coated papers was also investigated using corn oil. Overall, wax coating on the paper substrate showed its ability to cover and fill the voids of the paper. The oil contact angle improved after wax coating compared to the uncoated paper by a minimum ∼21% for beeswax and emulsion wax coatings and a maximum ∼35% for soywax and biowax coatings. The oil contact angle of wax-coated and uncoated paper observed in this study was close to the value reported in the literature for uncoated paper (<50°) and microcrystalline wax-coated paper (<60°),[23] respectively. The oil contact angle of wax-coated papers in this study was higher than those reported for stearic acid (an 18-chain saturated fatty acid)-chitosan double layer-coated paper[72] as well as paraffin wax emulsion-coated papers.[34]

Since waxes are hydrophobic, it is reasonable that a layer of hydrophobic wax on the paper will be lipophilic; thereby, a significant increase of oil contact angle was not observed after wax coating. Similar justification was reported in the literature

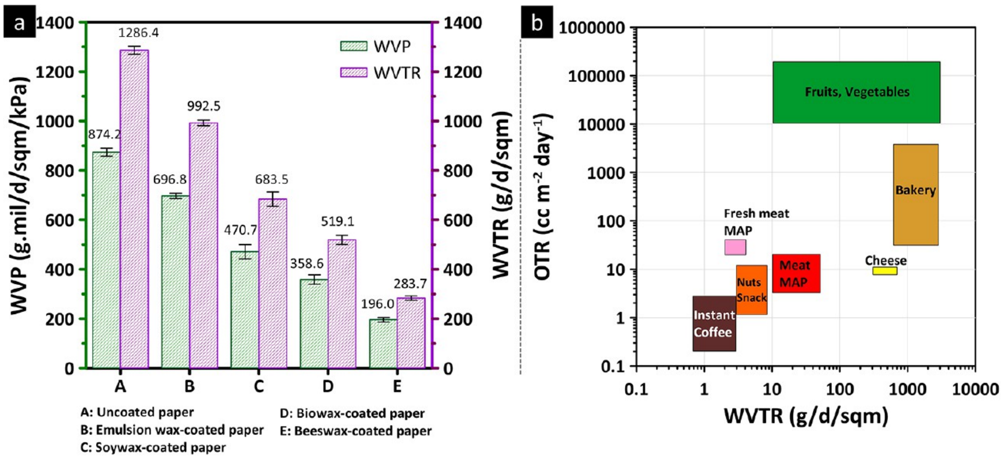


Figure 9. (a) Water vapor permeability and WVTR of uncoated paper and wax-coated papers. (b) OTR and WVTR requirements for various types of food products. The wax-coated papers developed in this study meet the WVTR requirements for packaging of fruits and vegetables (∼10−3000 g/m^2 day) as well as bakery products (∼620−2800 g/m^2 day). Panel (b) is redrawn by authors with permission under a Creative Commons [CC BY-NC-ND 4.0] from ref 78. Copyright [2021] [Elsevier].

after coating of a hydrophobic layer derived from a cross-linked copolymer of polydimethylsiloxane and tetramethoxysilane on the paper.[73] But still wax-coated paper could improve the oil contact angle compared to the uncoated paper by at least ∼10°.

4.2.3. Water Vapor Barrier Properties. Water vapor permeation is determined by how well water vapor dissolves in a polymer (i.e., solubility).[74] The chemical interaction between the polymer and the water vapor molecule influences the solubility function.[35] There are very few instances in the literature about investigating the influence of only wax coating on the water vapor barrier properties of the paper, which indicates the unexplored aspects of this field.

In this study, we could measure the barrier of wax-coated papers against water vapor using the gravimetric cup method (Figure 9a). This was advantageous as the WVTR of biowax-coated paper in the previous literature was reported to be immeasurable, probably due to presence of multiple cracks on the surface of the biowax-coated paper.[20] The WVP of a commercially available waxed paper (i.e., Reynolds Kitchens Cut-Rite) was also measured using the gravimetric cup method to compare the results with wax-coated papers developed in the present research.

The uncoated paper presented the highest permeability to water vapor due to a favorable chemical interaction between water vapor molecules (i.e., penetrant) and the hydroxyl groups (OH) of the cellulose paper. Coating waxes on the paper introduced hydrophobic characteristics into the cellulose fibers due to the long fatty acid chains of the wax structure, particularly in the case of beeswax, soywax, and biowax, thereby reducing the water vapor permeability. In addition, the wax coatings may fill in the void areas and block the pores of the paper, thereby preventing water from being absorbed. A similar theory was reported with soybean oil-based emulsion coatings on paperboard with a coating weight of 18−58 g/m^2.[13]

Among the wax-coated papers prepared in this study, beeswax coatings showed the highest barrier properties against water vapor. Overall, the percent improvement of water vapor barrier properties for wax-coated papers prepared in this study compared with the uncoated paper is in the following order: beeswax-coated paper (77.6%) > biowax-coated paper (59.0%) > soywax-coated paper (46.2%) > emulsion wax-coated paper (20.3%).

The different effects of these four waxes on water vapor barrier, WCA, and other characteristics of coated papers are attributed to the different chemical structures, represented in Table 1, of the utilized waxes and their hydrophobic characteristics.[34] In addition, percentage crystallinities of waxes, which were calculated by XRD, and their coating weight, are effective in water vapor barrier improvement of wax-coated papers. Higher degree of crystallinity and coating weight for beeswax resulted in a higher barrier against water vapor compared to the other three wax-coated papers.

Han et al. reported that beeswax remarkably improved the water vapor barrier properties of paperboard by 89%,[75] which is higher than the value obtained in this study for beeswax-coated paper. The difference might be due to the base substrate used by Han et al., which is a paperboard (with a thickness of 441.0 ± 0.7 μm) rather than the paper (with a thickness of 100 ± 0.00 μm) used in the present study. In addition, paperboard generally has a grammage of more than 250 g/m^2,[4] compared to the paper used in this study with a grammage of 40 g/m^2. Han et al.[75] further reported that coating of a whey protein isolate/cellulose film on the beeswax layer increased the barrier characteristics of paperboard in lower proportions in comparison with beeswax alone, confirming the superior ability of the beeswax as a lipid-based material in improving the barrier of the paperboard substrate against moisture.[75] Dip-coating of carnauba wax on the paper using micro- and nanoemulsion formulations improved the WVP of uncoated paper by ∼47 and ∼72%.[27] Compared with the percentage improvement of water vapor barrier results of our study, except for emulsion wax-coated paper, the other three waxes (bees, soy, and biowax) showed similar values to the carnaubawax-coated on the paper, with beeswax-coated paper showing superior ability in improving the water vapor barrier (∼77%). It is noteworthy that we coated waxes on the both sides of the paper only one time as opposed to 5 times coating carnauba wax on the cellulose sheets.[27]

Although the coating appearance of wax emulsion seemed uniform in SEM images, the water vapor barrier properties of emulsion wax-coated paper were inferior to those of the other three wax-coated papers. The possible reasons can be as follows: (i) although the water emulsion wax-coated paper was dried after coating, it is possible that some water molecules trapped in between CH_2-CH_2 chains make it favorable for permeation of water molecules through the wax emulsion-coated papers, and the curling and shrinkage of emulsion wax-coated paper observed right after coating and drying, respectively, can be the sign of trapped water molecules between the CH_2-CH_2 chains of the wax emulsion, (ii) the presence of COO− and C−O−C groups in the chemical structure of other three waxes (Table 1) in contrast with emulsion wax may contribute to H bonding with the OH groups of cellulosic paper, thereby increasing the adhesion between wax and paper and leading to a higher barrier against water vapor in contrast with the inferior barrier of emulsion wax-coated paper, and (iii) the lower coating weight of emulsion wax than other three waxes can lead to an inferior water vapor barrier.

Lastly, the structure of the coating and its uniformity significantly affect the penetration and absorption of water into the paper.[34] As was observed from the SEM images, waxes impregnated into the paper fibers resulted in a reduction of the paper porous structure and the possibility of waxes acting as a binder between cellulosic fibers. This indeed can make it harder for penetration of water molecules into the paper, thus improving the barrier against WVP. Nowacka et al.[34] also reported that paper and paperboard impregnated with the paraffin wax emulsion characterized as having better water vapor barrier properties and resistance against water and oil compared with the uncoated samples.

The positive effect of wax incorporation in coating formulations for paper-based substrates has been observed in the literature. For example, Bayés et al.[16] emphasized that the improved barrier properties of paper-coated with beeswax-water emulsion stabilized with cellulose nanofibers (<100 g m^{-2} d^{-1}) cannot be explained without beeswax, which shows the importance of the beeswax hydrophobic component in the coating formulation. In another effort, when 20 wt % beeswax was incorporated in hydroxypropyl methyl cellulose (HPMC)-glycerol coating formulations, the coated papers showed better water vapor barrier properties than those formulations without beeswax.[76] Nonetheless, the percentage water vapor barrier improvement (∼20%) for beeswax-HPMC-glycerol-coated paper compared to uncoated paper was lower than the results obtained in the present study (∼77%). Paper-coated with acrylated linseed oil reduced the WVTR by ∼64% due to the hydrophobic long aliphatic chain of linseed oil. Additions of 3 wt % beeswax to the acrylated linseed oil and coating on the paper resulted in further reduction of WVTR (by ∼50%), while adding more beeswax (15 wt %) increased the WVTR due to the beeswax aggregation, phase separation, and nonuniform coating.[21] In comparison with paraffin wax emulsion-coated paper, which reduced WVP by ∼30%,[34] the wax-coated papers in the present study showed superior ability in reduction of WVP, except for emulsion wax-coated paper, which could reduce the WVP of uncoated paper by only 20%.

The water vapor barrier properties of a commercial wax-coated paper were also measured with the gravimetric cup method in this study. Wax-coated papers prepared in this study showed higher WVP and WVTR values compared with Reynolds commercial wax-coated paper (WVP of 25.56 ± 0.50 g mil/d/sqm/kPa and WVTR of 103.89 ± 1.07 g/d/sqm), which can be due to the paper type and the wax used in the Reynolds commercial paper as well as the coating method. The wax-coated papers developed in this study showed a promising barrier against water vapor which meet the WVTR requirements for packaging of fruits and vegetables as well as bakery products.[77−79] As it is shown in Figure 9b, fruit−vegetable and bakery product packaging requires WVTR in the range of ∼10−3000 g/m^2 day and ∼620−2800 g/m^2 day, respectively. The wax-coated paper developed in this study showed the WVTR in the range of 283.7−992.5 g/m^2 day (Figure 9a).

Overall, natural waxes that have low affinity for water inhibit the moisture permeation through the cellulose fibers that act as a path for moisture penetration into the paper.[80] Substitution of current synthetic nonbiodegradable waxes with more environmentally friendly waxes (biowax, beeswax, and soywax) used in this study can contribute to less packaging waste through a circular economy.

4.2.4. Mechanical Properties. The mechanical properties of biomaterials should be evaluated while using them as a coating material for paper, as they are significantly different from synthetic polymers such as polypropylene, PE, and paraffin wax, which is widely used in the paper coating industry.[9] Therefore, we investigated the effect of wax coating on the tensile strength (TS), percent elongation at break (EB %), and Young's modulus (E), which is depicted in Figure 10.

Paper, whose main constituents are natural carbohydrate polymers, provides sufficient physical strength properties. However, its porosity and hydrophilic properties can lead to water absorption from food or the surrounding environment. This, therefore, may cause mechanical strength loss of the paper and create suitable conditions for growth of microorganisms.[81] Paper strength is influenced by factors such as fiber length, strength, and interfibrillar forces.[82] The impact of adding lipids to films and coatings on their mechanical strength depends on various factors, including the type, quantity, and physical state of the lipid phase, as well as the polymer type and the film production method.[83]

Uniaxial-tension tests in the machine direction were performed to measure the tensile properties of the paper. In the case of all four waxes, the TS and modulus of wax-coated samples increased compared to those of the uncoated paper, in which beeswax-coated paper exhibited the highest percentage of improvement in TS (∼26%) and modulus of elasticity (∼46%). Several papers reported a reduction of mechanical strength because of biopolymer-wax coatings on the paper substrates.[27,84] A reduction in elastic modulus was reported after micro- and nanocarnauba wax emulsions were coated on cellulose sheets[27] as opposed to the present study. On the other hand, some literature reported that wax incorporation in the paper coating formulation showed no effects on the TS of the paper.[83,85] They elaborated that this is due to the relatively low coating weights in comparison to the grammage of the paper and the TS for the coated paper was controlled by the TS of the base paper.[86]

However, we did not observe these behaviors in the case of TS and modulus as both of them increased as a result of wax coating on the paper. The wax coating fully penetrated into the paper and increased the thickness, which could result in an increase in the elastic modulus through the change in geometry. Similar to our results, Vijayan et al.[21] observed that after adding beeswax to the acrylate linseed oil coatings on the paper, TS increased. This might be due to the percolation

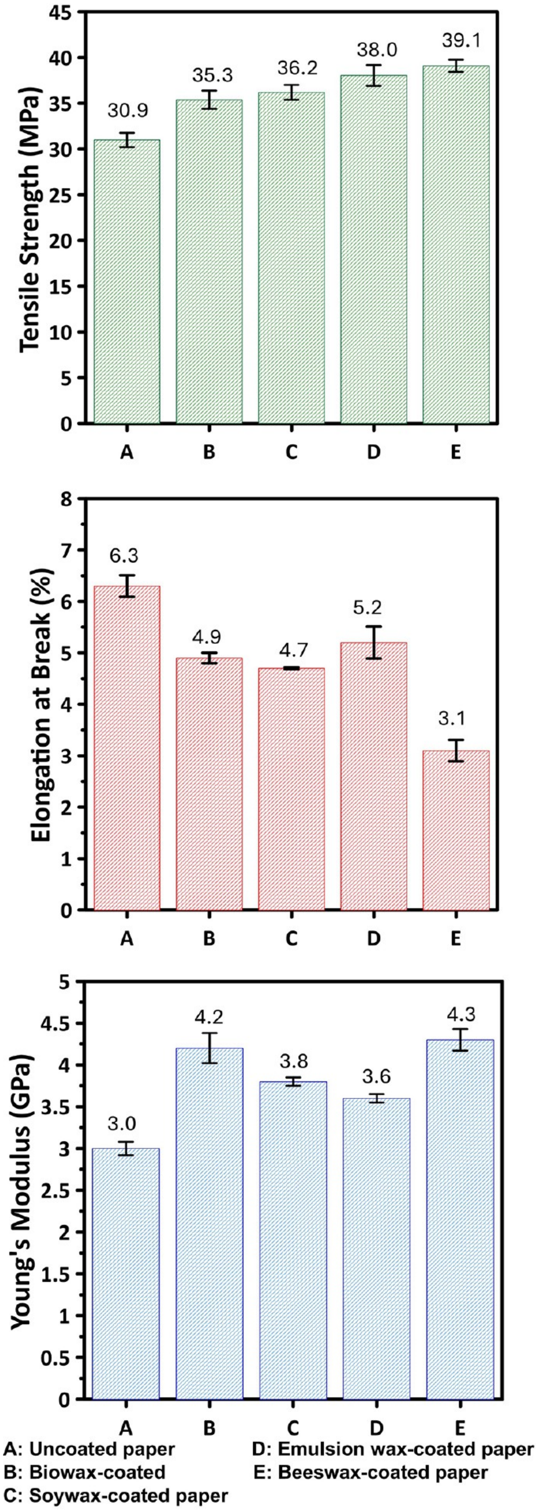


Figure 10. Mechanical properties of the uncoated paper and wax-coated papers.

of wax coating into the cellulosic fibers, as was also observed in the SEM images, and it acting as a binder between cellulose fibers, resulting in improvement of tenacity, strength, and stiffness of the paper. A similar observation was reported after coating paper sheets with chitosan.[83]

In terms of elongation at break, we observed a reduction after wax-coating the paper for all four waxes compared to the uncoated paper. Similar reduction in elongation at break was reported after coating of carnauba wax nano- and micro-emulsion on Curaua cellulose sheets.[27] Similarly, the addition of beeswax into the acrylated linseed oil coatings reduced the elongation at break.[21] Further, Vijayan et al.[21] explained that increasing the addition of beeswax more than 10 wt % into the linseed oil coating formulations resulted in beeswax aggregation and reduced elongation at break. This may happen in our case for the beeswax coating (lower elongation at break) compared to soy, emulsion, and bio wax coating with higher elongation at break. Also, waxes are crystalline substances, as observed in the POM micrographs as well as in XRD spectroscopy. High crystallinity of waxes can contribute to brittleness of wax-coated paper and reduction of elongation at break compared to uncoated paper. In contrast to our study, an increase in the elongation at break of a maleated camelina oil-coated paper was reported in comparison with uncoated paper due to the possible cross-linking between the coating and cellulose paper.[87] Although the maleated camelina oil is reported as a potential sustainable biodegradable coating material,[87] no information was reported about biodegradability of paper-coated with this oil. It is noteworthy that possible cross-linking between any coating material and the paper substrate can have a negative effect on the biodegradation of the coated paper, which is not desirable.

Finally, the mechanical properties of wax-coated papers in this study were comparable to some commercial papers investigated by Gücüş et al.[88] which reported the elastic modulus of 3600 and 5900 MPa and an elongation at break of 1% and 4.1%, for wrapping paper and sulphite paper, respectively.

4.2.5. Oil Absorption Test within a Real-Life Application.

To evaluate the oil-resistance capability of wax-coated papers prepared in this study, a drop of 2 μL was placed on the wax-coated papers (5 × 5 cm), as depicted in Table S1. After 8 h, the oil drop was wiped from the uncoated and wax-coated paper samples using a clean tissue, and the oil absorption was calculated based on eq 3 in Section 3.8 and the results are summarized in Table 6. Wax coating reduced the oil absorption of the paper substrate significantly. Emulsion wax coating showed ∼59% reduction and soywax, biowax, and beeswax coatings showed ∼70% reduction in the oil absorption. This indicates the potential application of these oil-repellent wax-coated papers for food packaging of oily food. Similarly, the beeswax coating showed resistance against grease permeation of coated papers.[14]

Table 6. Oil Absorption of Uncoated and Wax-Coated Papers Using Corn Oil

sample	weight % oil absorption
uncoated paper	99.24%
emulsion wax-coated paper	40.83%
soywax-coated paper	29.38%
biowax-coated paper	29.18%
beeswax-coated paper	29.12%

To simulate real-life applications involving wax-coated papers, we created food boxes using both uncoated and wax-coated paper samples. These boxes were then filled with fried potatoes bought from the market and the staining of oil on the box's backside was monitored visually for 24 h. As shown in Figure 11, the beeswax-coated paper demonstrated the best performance in terms of oil-resistance properties. Up to 7 h, no

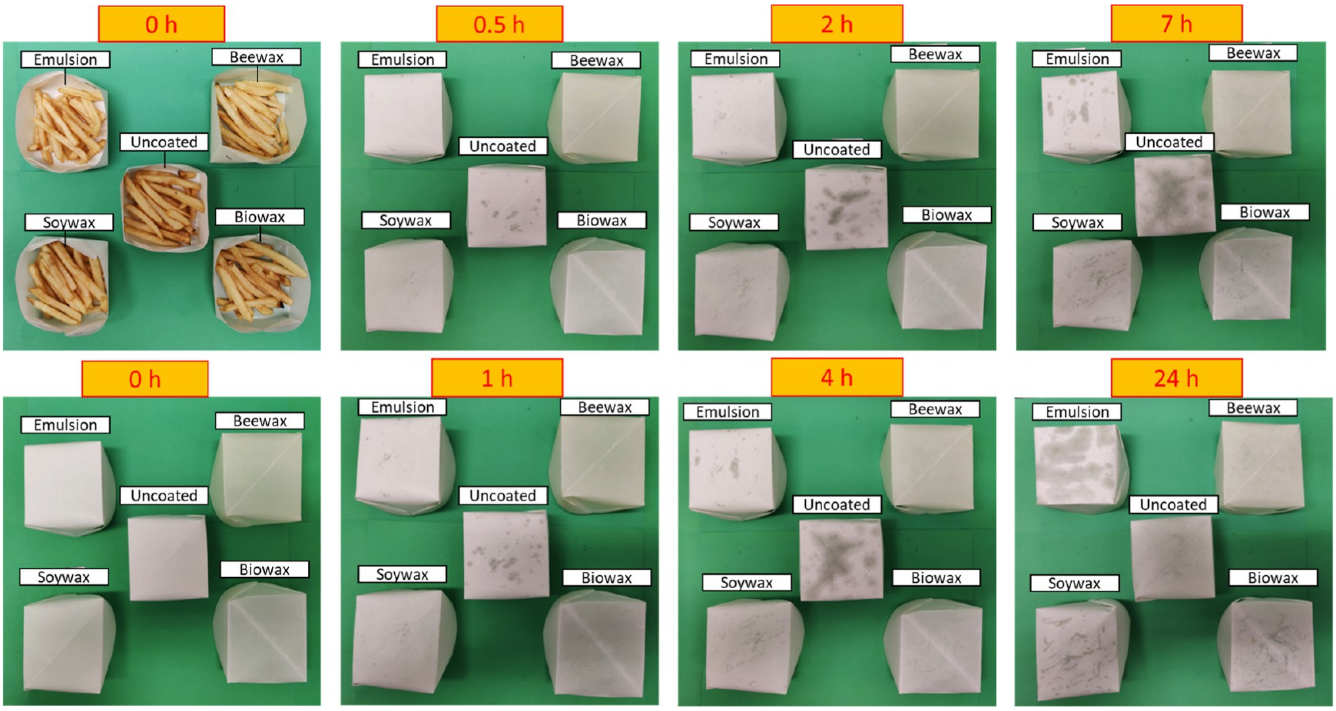


Figure 11. Oil absorption-staining experiment. The fried potato was used to monitor the oil staining on the boxes made from uncoated paper as well as wax-coated paper to simulate real-use application of wax-coated papers in food packaging of oily food.

stain was observed on the beeswax-coated box, while after 24 h, slight oil staining (no leaching) was observed, in contrast to the uncoated paper that fully absorbed the oil after 24 h (included leaching). The oil-resistance capability for wax-coated boxes was in the following order, which is in accordance with the calculated oil absorption values, reported in Table 6.

Beeswax-coated box > biowax-coated box > soywax-coated box > emulsion wax-coated box.

Overall, among the wax-coated papers, beeswax and biowax were the best in terms of resistance against oil, which showed the least absorbed and oil stain. Zhang et al.[14] also reported that chitosan-beeswax coating on the paper improved the grease resistance of paper as the grease resistance increased compared to only chitosan-coated paper. Generally, waxed paper is commonly used to package bread, dairy products (such as milk and cream), biscuits, cakes, sandwiches, breakfast cereals, and sunflower oil and in paper bags known as "carry out" and "carry home".[4] It is important to note that before commercial use, wax-coated papers should be evaluated for migration values according to standard test methods to ensure food safety. Based on the standard test methods EN 1186-1:2002 and EN Regulation No 10/2011, the overall migration limit from packaging materials is 10 mg/dm^2 of food. Liu et al.[23] reported that, when the coating weight of microcrystalline wax on the paper was more than 6 g/m^2, the migration value in the food simulant could surpass the limit. Similarly, the coating weight of 6 g/m^2 paraffin wax emulsion on the paper showed migration values less than 10 mg/dm^2.[34] Since the wax-coating weight in the present study was less than 6 g/m^2, the overall migration value is expected to be lower than the limit. Nevertheless, it is necessary to assess the migration values prior to practical applications.

5. CONCLUSIONS

In summary, our study aimed to enhance the barrier properties of a paper substrate by using the bar-coating technique to apply four different waxes. The bar-coating technique led to a uniform coating and reduced paper porosity, resulting in an improved water vapor barrier and water and oil contact angle compared to uncoated paper. SEM studies showed that beeswax and emulsion wax better filled paper pores, yet emulsion wax exhibited the weakest water vapor barrier. XRD and POM studies confirmed the highly crystalline structure of waxes, which contribute to enhanced barrier properties. The beeswax-coated paper showed the highest barrier against WVP owing to its higher coating weight and degree of crystallinity. Wax coatings improved the paper's TS and elastic modulus, though they reduced the elongation at break. Developing wax-based biocomposites could enhance adhesion and counter brittleness, further improving mechanical and barrier properties.

Waxed paper has potential applications for extending the shelf life of packaged foods, but further studies are needed, including compostability of wax-coated papers and migration values for commercial use. The approach of this study is advantageous for its lack of fluorochemicals and organic solvents, aligning with sustainability goals. The food packaging sector could benefit economically and environmentally from replacing petroleum-based coatings with ecofriendly waxes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenvironau.4c00055.

Additional experimental photographs of the oil absorption test for uncoated and wax-coated papers (PDF)

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Notes

The authors declare no competing financial interest.

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This paper was published ASAP on December 17, 2024, with an error in Table 1. The corrected version was reposted December 26, 2024.